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Banded spherulites of HDPE molded by gas-assisted and conventional injection molding

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ABSTRACT

Crystal morphologies of high density polyethylene (HDPE) with low molecular weight obtained by gas-assisted injection molding (GAIM), conventional injection molding (CIM), and spontaneous cooling, respectively, were studied by scanning electronic microscopy (SEM). It is found that banded spherulites are generated in the inner zone of GAIM parts and the outer zone of CIM parts but are absent in quiescent parts. According to the results, the representative morphologies of crystal change with gradual increment of instantaneous flow field in crystallization from non-banded spherulite to banded spherulite and then to oriented lamellae. This morphological evolution indicates that banded spherulites could be induced by flow field with certain intensity, which is confined by both an upper critical value and a lower one.

1. Introduction

It is well known that polymer crystallization in processing could be influenced by the operating conditions such as flow rate and strain, due to the flow fields imposed on the polymer melt during molding process [1,2]. So far, great efforts have been dedicated to the studies of polymer crystallization in external flow field, and two typical crystal morphologies were reported as flow-induced oriented ones (e.g. shish–kebabs) and spherulites [3–6]. Even though non-banded spherulites are commonly observed in molding process, spherulites exhibiting bands are rarely reported in polymer processing. In fact, they could also be gained in flow field [7] but the intensive research on banded spherulites has been generally made in the quiescent state. Being characterized with alternating edge-on and flat-on lamellae, the presence of banding in polymer spherulites is generally attributable to a twisting of crystallographic orientation along the radial direction of the spherulites [8–11]. However, the effect of mechanical field on the banded spherulite formation and why crystalline lamellae twist in the banded spherulites are still unclear.

Recently, we have carried out intensive investigation on polyolefin achieved by gas-assisted injection molding (GAIM) [12,13]. The main feature of GAIM is that the mold cavity is partially filled with polymer melt, and then compressed gas penetrates the molten polymer and drives it further into the mold end until the cavity is completely occupied. The polymer melt in the GAIM process is confined by both the mold wall and the compressed gas, and is subjected to severe instantaneous flow field during the gas penetration stage, which is more complicated than conventional injection molding (CIM) process. In previous work we investigated the crystal morphology of high-molecular weight HDPE in GAIM, based on the consensus conclusion that polymers with higher molecular weight are more sensitive to flow field than the lower ones [14,15]. It was reported that the GAIM part is characterized with hierarchical crystalline morphologies through the thickness, including a highly oriented skin with parallel lamella stacks, a shish–kebab structured sub-skin, and a typically spherulitic core [13]. In order to systematically understand the relationship between shear intensity, molecular weight and flow induced microstructure in GAIM as a long-term project, research on HDPE with series of molecular weights is one of the necessary subjects. In this communication, the crystal morphology of low molecular weight HDPE obtained via GAIM is investigated based on the previous work. For comparison, the crystal morphologies of the same material obtained by CIM and quiescent melt-crystallization were also studied. Since banded spherulites in GAIM and CIM have never been reported up to now, our work represent the effect of instantaneous shear field on banded spherulite formation and provide a new opportunity to understand fundamental issues about the mechanism of lamellar twisting in banded spherulites.

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2. Experimental section

2.1. Materials

High density polyethylene (HDPE 2911) ($M_w = 1.4 \times 10^5$ g/mol) with a melt flow rate of 20 g/10 min(190 °C/2.16 kg, ASTM D1238) and a density of 0.960 g/cm^3, was supplied by Fushun Petrochemical Corp.

2.2. Sample preparation

The quiescent specimens were prepared by cooling the granular materials from 195 °C to 10 °C (the room temperature) spontaneously after 5 min of constant temperature melting.

A Grand 140–320 injection molding machine was employed for the dynamic specimens molded in the processing fields. During GAIM process, high pressure nitrogen was injected by a gas injection system (model MPC). In order to provide a routeway for gas penetration, the main bodies of both the GAIM and CIM parts were designed in a columned shape, as referred in literature [12]. The difference between them is that the CIM part exhibits a solid structure while the GAIM one shows a hollowed gas channel.

The highest temperature in the temperature profile of the injection molding machine was 195 °C. The mold temperature was about 30 °C. Other detailed experimental procedures and conditions in GAIM molding can be found in Ref. [13]. The CIM process was carried out by using the same processing parameters, except that the melt in CIM process was not exposed to gas penetration and gas-assisted packing process. Thus, it should be noted that the melt injection volume for CIM was as large as 100 vol%.

2.3. Scanning electron microscopy (SEM)

The specimens were characterized via SEM after selective permanganic etching. Before etching, the segments which are 5 mm long in the middle of GAIM and CIM parts were cut, then cryogenically fractured parallel to flow direction in liquid nitrogen. The selected regions in CIM and GAIM parts for observation are illustrated in Fig. 1. For the observation of crystal morphology, all specimens were etched by permanganic etching technique [16]. After the surfaces were covered with a thin layer of gold, the crystalline morphology in different zones of these parts was observed by a SEM instrument, JSM-5900LV, operating at 20 kV.

3. Results and discussion

3.1. The effect of gas penetration on crystal morphology

Fig. 2 shows representative SEM micrographs of crystal morphology in different zones of the etched HDPE molded by GAIM. They are quite different from the counterparts with higher macromolecular weight ($M_w = 5.28 \times 10^5$ g/mol) in previous work, which have, respectively, parallel lamella stacks and shish–kebab in the outer zones, and the common spherulites in the inner zones [13]. Without the appearance of shish–kebab structure, the outer zones of these GAIM parts sketched in Fig. 2(c) are dominated by parallel lamella stacks, perpendicular to the melt flow direction, as shown in (a). This is ascribed to a critical molecular weight that is needed for shish–kebab to be effectively induced at a given shear rate [17,18]. Only when the polymer macromolecular weight is larger than the critical value, the shish–kebab structure could be induced in certain flow field. The thickness of the outer zone is about 200 μm (Fig. 2(c)) along the residual thickness direction (the whole thickness of GAIM part is about 1500 μm. Crystal morphology has always hardly been observed in the 50 μm outer skin of both parts molded by CIM and GAIM, for the possible reasons of etching effect and small quantity of crystal. Therefore, the description in this paper has excluded this skin layer when referring to ‘the outer zone’ for the sake of brevity).

Most interestingly, one can observe a large number of well-developed banded spherulites going inwards from the interface which is about 200 μm from the outer skin to the inner skin close to gas channel (Fig. 2(b)). Meanwhile, it should be noted that the width of banded spherulite region could be influenced by the processing parameters. To the best of our knowledge, this morphology intensively reported in quiescent melt-crystallization process is observed in GAIM for the first time and seldom reported in other polymer processing methods. In the inner zone, the number and perfection of the banded spherulites vary in the radial direction, as shown in Fig. 3. As the distance from the inner skin close to gas channel decreased from1000 μm (Fig. 3(a)) to 500 μm (b) and then to 100 μm (c), the corresponding radiuses of banded spherulites are 55–85 μm, 35–60 μm and 25–40 μm. However, the distribution density of banded spherulites has an inverse relation with the radius along the residual thickness direction. The change in the radius and density of banded spherulites in the radial direction is the result of the complex thermo-mechanical field gradient [7], which was discussed in subsequent sections.

To obtain a detailed description of the fully grown banded spherulites, the banded spherulites in GAIM parts are investigated by SEM with high magnification, as shown in Fig. 4(a) and (b). Due to the easier dissolution of polymer chains at lamella edges and the different effects of etching between edge-on and flat-on lamellae [19–21], the flat-on lamellae can hardly be observed in the valley regions of the bands, while the edge-on ones are distinctly shown in the bright bands, i.e. the peak zones (Fig. 4(a)). Moreover, in the morphology shown in Fig. 4(b), the lamellae having S- or C-shaped profiles are observed as the pronounced dominant molecular architectures in bright bands, which is primely consistent with other reports [6,8]. These detailed profiles of the curved lamellae are well in line with the features that twisting occurs in the radially grown lamellae of banded spherulites.

Since lamellar twisting has seldom been reported in polymer molding process, the crystal morphologies in the CIM parts with the GAIM parts were compared to explore the effect of gas penetration on the banded spherulite formation. Fig. 5 shows the SEM micrographs of etched surface of HDPE molded by CIM. In Fig. 5(a), unlike the homogeneous distribution of banded spherulites in GAIM parts, banded spherulites in the outer zone of CIM parts are occasionally presented in the form of agglomerates. The thickness of banded spherulites rich zone in CIM parts is about 250 μm in the radial direction and the cross-section diameter of CIM part is about 8 mm, as shown in Fig. 5(c). As for the inner zone, typically common spherulites (non-banded) which have been universally observed as reported in large number of literatures randomly exist in the core of the CIM parts [1,2], with the diameters that ranged from 15 μm to 25 μm, as shown in Fig. 5(b). However, what attracted our very attention and interest is the location of banded spherulites in CIM parts (Fig. 5), combined with the crystal morphology evolution

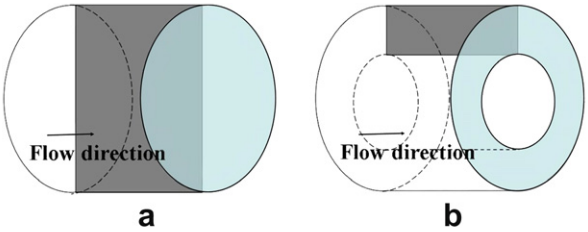

Fig. 1. SEM observation surface (in gray) of HDPE molded by CIM and GAIM. (a) CIM part; (b) GAIM part.

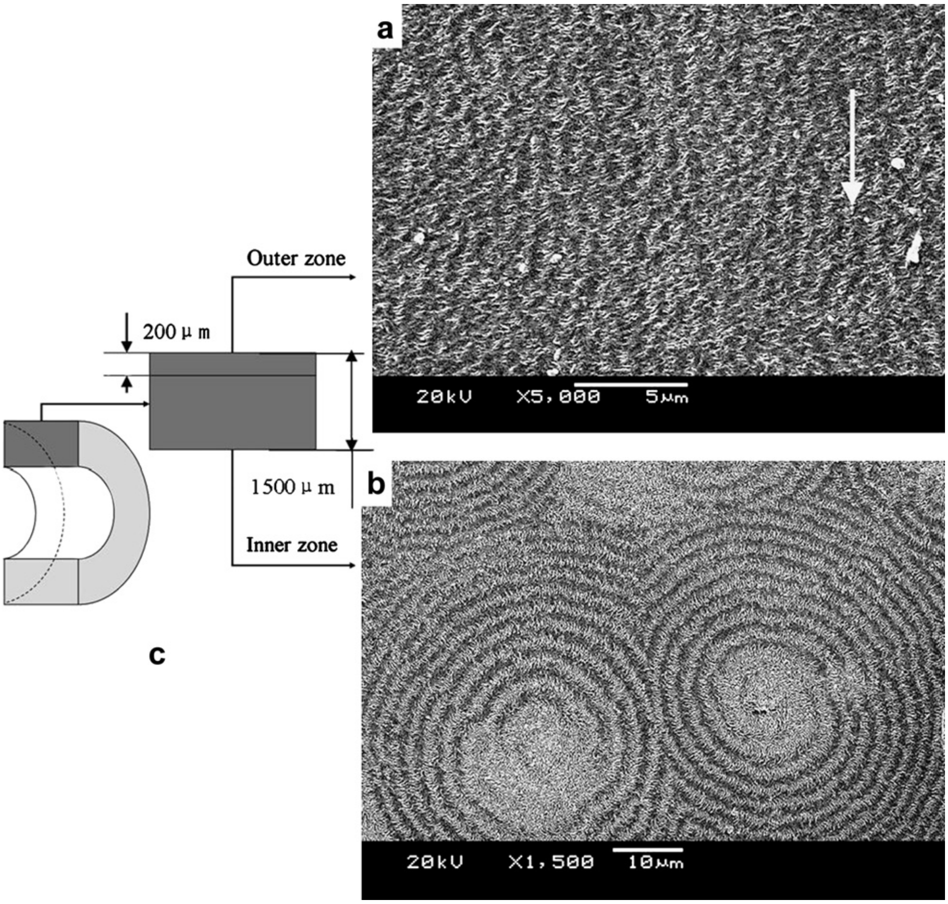

Fig. 2. SEM micrographs of the crystal morphologies in different zones of HDPE molded by GAIM. (a) Outer zone; (b) inner zone; (c) schematic representation of zone distribution, the arrows represent flow direction.

in the radial direction of GAIM parts (Fig. 2(a) and (b)). The intensity of the flow fields ranked as in the gas channel zone of GAIM parts, followed by the outer zone and the core zone of CIM parts in turn. That is because the flow field could be reinforced by gas penetration when the polymer melt was pushed along the flow direction by the compressed gas [13] and there is shear gradient in the CIM polymer melt from the skin to the core zone. A question arose that if the banded spherulites can be induced by certain flow field.

To make the problem clear that how the flow field affected the formation of banded spherulites, the crystalline morphology of quiescent melt-crystallized specimens was also studied. As shown in Fig. 6, no more banded spherulites are observed on the whole etched surfaces of specimens, which were cooled spontaneously from the same melt temperature as GAIM and CIM ones but without any shear stress exerted. The anticipated absence of banding in the crystalline morphology of quiescent melt-crystallized specimens confirms the inducing effect of flow field on banded spherulite formation. This result indicates that a lower critical intensity of the flow field was indispensable to effectively inducing banded spherulites. However, it is not certain that banded spherulites can always be induced as the continual increase of shear intensity, according to the emergence of oriented lamellae in the outer zone of GAIM part (Fig. 2(a)). In the outer zone, where the fast flow rate was exhibited along the whole depth direction, the chain segments are partly induced to align in the flow direction, which results in the oriented lamellae growing in the perpendicular direction to flow [22]. Therefore, there is also an upper critical intensity of the flow field, and only when the actual value of the flow field intensity was in this range, polymer crystal can be generated in the form of banded spherulites.

According to the variety of banded spherulites in flow fields with different shear intensities, the formation mechanism of banded spherulites in flow field can be drawn as follows. In CIM and GAIM processes, in spite of the fast cooling caused by contact of polymer melt with the mold wall or/and the cold gas, the temperature of most polymer melt is higher than the crystallization temperature, when instantaneous exoteric shear and stress are exerted during the melt injection and gas penetration stages. Therefore, the latter growth period of spherulites i.e. the lamellar radial advance in the three types of specimens is similar in static circumstance, which means it is the initial crystallization stage that overwhelmingly decides the formation of banded spherulites, namely the origin of lamellar twist lies in the crystalline core or the initial fold surface.

Accordingly, five steps are involved to depict the formation process of banded spherulites in flow field, and the former four are shown in Fig. 7.

(1) At the initial cooling stage, the polymer melt is exposed to flow field, which is composed of millions of micro-fields with melt fluctuation and mechanical shearing. Because of the great change in local density and concentration, much more intensive thermal, mechanical or compositional fields could be induced in the crystal growth front than those generated in quiescent melt [10]. Therefore, the random coil in polymer melt would be ordered in these micro-fields (Fig. 7(a)).
(2) At the initial crystallization stage, the fold packing is affected by the strong local micro-flow fields so that great fold surface stress is accumulated in the incipient lamella fold (Fig. 7(b)).

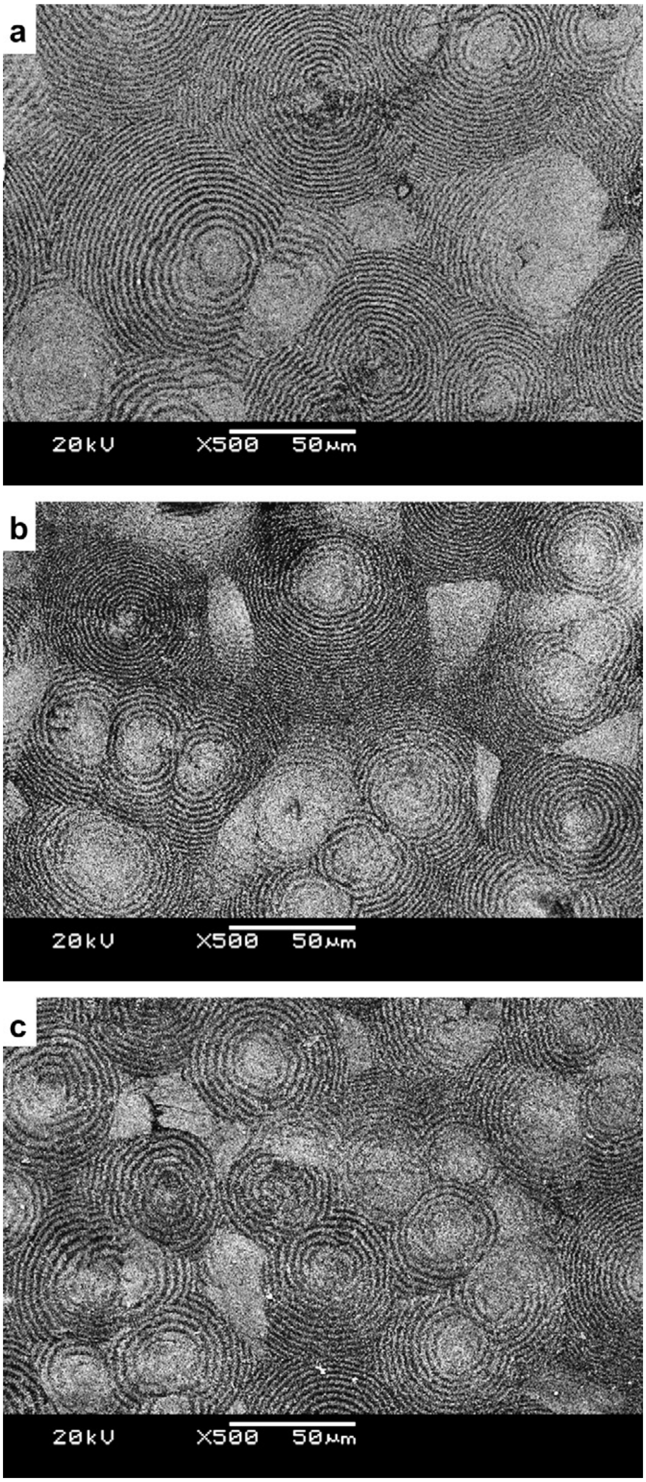

Fig. 3. SEM micrographs of the crystal morphologies in different layers of the banded spherulite zone in GAIM parts. (a) 1000 μm; (b) 500 μm; (c) 100 μm, from the inner skin close to gas channel.

(3) In the succedent lamellar growth, fold surface ordering is induced to relieve the fold surface stress. As a result, the chains which are essentially parallel to lamellar normal change to be inclined (Fig. 7(c)) in the lamellae, which introduces the essential asymmetry into the system.

(4) When the magnitude and gradient of the field are larger than the elastic resistance, which means that the stress is sufficiently high to produce inclined fold surfaces, the lamellae become twisted (Fig. 7(d)) so that they grow in intimate contact with the affected substrate are induced to move portions of the growth face to regions of lower stress in the melt, as simulated by Schultz [10]. Meanwhile, the twisting is amplified by the formation of giant screw dislocations, systematically to one side of the S for a given radius, giving diagonal linkages and each developing lamella a comparatively large increment of twist [9].

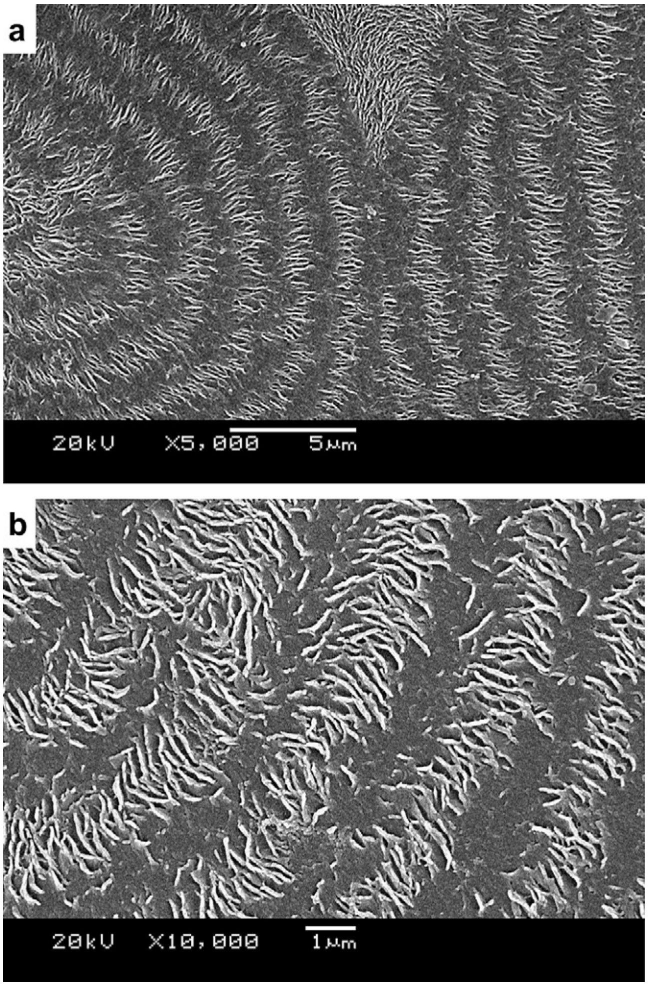

Fig. 4. SEM micrographs with high magnification to represent the fine lamellar structure of banded spherulites in the GAIM parts. (a) 5000×; (b) 10 000×.

(5) Banded spherulites are generated, because the twisting growth keeps on spontaneously once the crystal twisting begins at the initial stage of crystallization process [8,23].

On the other hand, it should be noticed that the radius distribution of banded spherulites in GAIM and CIM parts is different. The banded spherulites dispersed in the outer zones of CIM part have the radius in the range between 35 μm and 50 μm, while the radius of those in the inner zones of GAIM parts increases in the outward direction in the range of 25–85 μm (Fig. 2(b)). Meanwhile, it is found that the non-banded spherulites encircled by random lamellae and amorphous regions in the quiescent melt-crystallized specimens (Fig. 6) are quite immature, with the diameters range from 3 μm to 5 μm. They are much smaller than banded spherulites and the non-banded spherulites in CIM parts. The great difference between the radiuses of non-banded and banded spherulites could be understood as follows. In the formation process of banded spherulites, since the banding can be driven by self-induced field in the growing front, the twisting lamellae bend to move the growth front into regions of lower field values [24]. Therefore, the growth

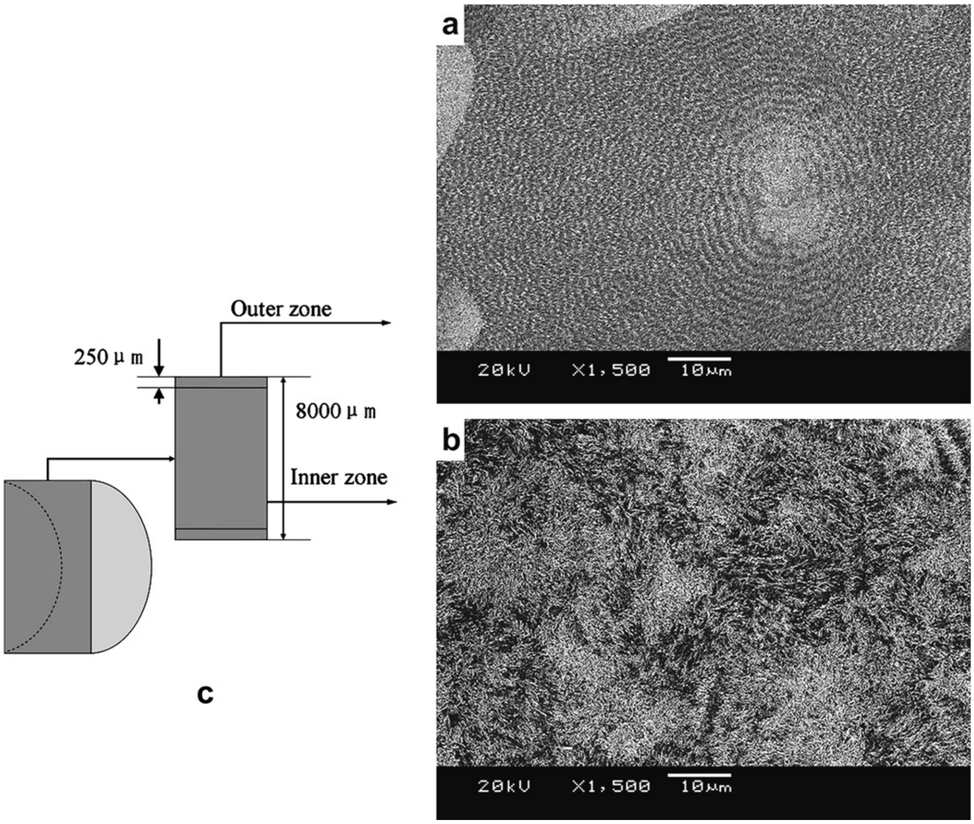

Fig. 5. SEM micrographs of the crystal morphologies in different zones of HDPE molded by CIM. (a) Outer zone; (b) inner zone; (c) schematic representation of zone distribution.

rate of twisting lamellae increased rapidly and the process would occur spontaneously, which causes that the radiuses of banded spherulites are much larger than that of non-banded ones [25,26]. Moreover, the difference in the radiuses of non-banded spherulites between CIM parts and static samples indicates that the absence of the ring pattern in spherulites is not a sufficient criterion to rule out twisting, i.e. lamellar twisting maybe exist in the core of CIM parts but it is too weak to manifest in the form of banding, as suggested by Lotz [27]. Only when the extent of lamellar twisting induced by the micro-field exceeds the critical value, the bands can be observed. This is consistent with the fact that banded spherulites can be induced by flow field with sufficient intensity.

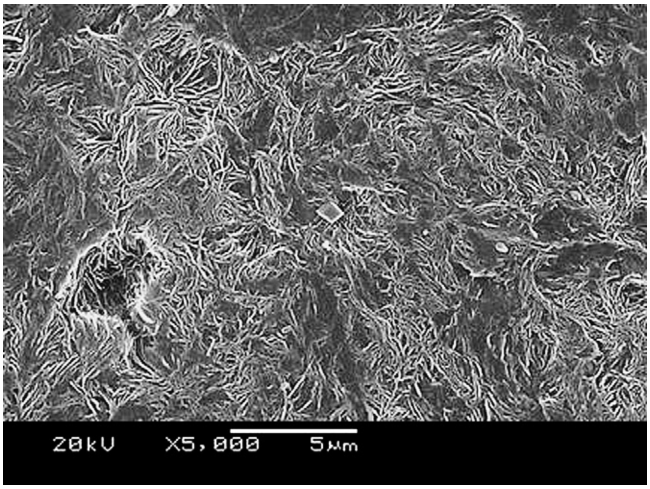

Fig. 6. SEM micrographs of the crystal morphologies of quiescently crystallized HDPE.

Now, it is clear that the development of the crystal morphology is strongly dependent on the gradually increasing flow field, listed as common spherulites → banded spherulites → oriented lamellae. For the three representative types of crystalline morphology, the schematic representation is illustrated in Fig. 8. What should be emphasized here was the concurrence of the upper and lower critical intensities of the flow field for banded spherulites to be effectively induced. Banded spherulites, as shown in Fig. 8(b), can be induced when polymer melt is subjected to flow field with the appropriate intensity confined by the two critical values. Since banded spherulites are the manifestation of lamellar twisting which is fierce enough [27], a lower critical flow intensity is required in the initial crystallization stage for the onset of eligible lamellar twisting. Otherwise, the lamellae in spherulites grow

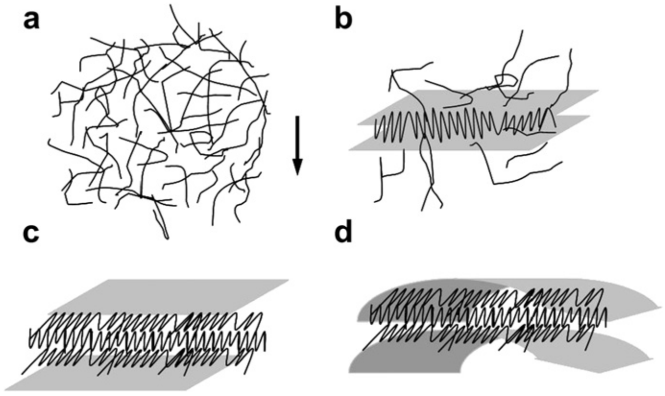

Fig. 7. Schematic representation of banded spherulite formation mechanism: (a) random coil in polymer melt with flow field (the arrows represent flow direction); (b) the incipient lamella fold; (c) fold surface ordering in lamellar growth (chain tilting); (d) lamellar twisting.

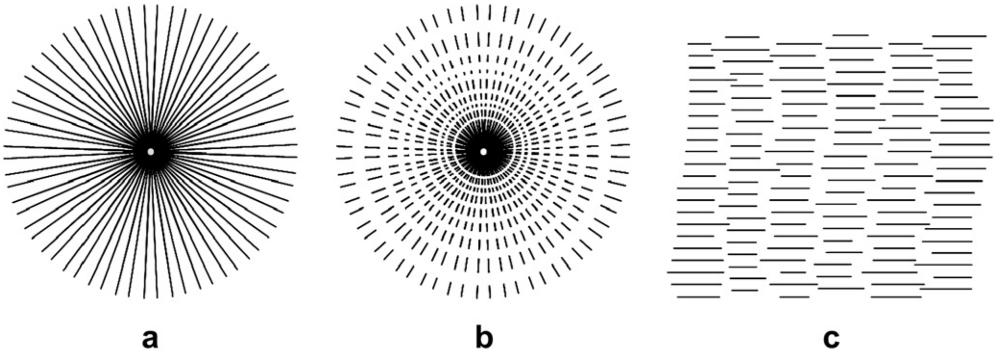

Fig. 8. Schematic representation of crystal morphologies changed with flow field: (a) quiescent; (b) weak shear; (c) strong shear.

radially without banding as shown in Fig. 8(a). However, when the polymer melt is exposed to a flow field with shear stress exceeding the upper critical value, some chain segments are aligned in the flow direction, which causes the crystalline precursors develop into oriented lamellae perpendicular to the shear flow (Fig. 8(c)) [22].

4. Conclusion

In the GAIM parts, well-developed banded spherulites are formed in low molecular weight HDPE, which is different from the ones with high molecular weight. According to the samples obtained by CIM, GAIM, and spontaneous cooling, the crystal morphologies present themselves orderly as non-banded spherulites, banded spherulites, and oriented lamellae, as the gradual increment of flow field in the crystallization process. Both an upper and a lower critical intensities of the flow field are necessary to effectively induce the banded spherulites. The crucial period for bands generating is concluded to be the initial crystallization stage, when the local field in the growth front is intensified by the flow field to overcome the elastic resistance to induce lamellar twisting. Since banded spherulites in polymers molding process are not universally studied, our work provide a new understanding of the formation of banded spherulites and benefit the elucidation of lamellar twisting mechanism.

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